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(54) PRODUCTION OF SILICA-ALUMINA COMBINED POWDER

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PURPOSE: To obtain silica-alumina combined powder having particle size in a submicron range and high purity, by hydrolyzing a mixed soln. contg. partial hydrolyzate of org. silicon compd. and hydrolyzable org. aluminum compd. in a specified proportion with adding to water or a hydrous solvent having a specified pH value.

CONSTITUTION: The mixed soln. of the partial hydrolyzate of hydrolyzable org. silicon compd. and 0.3-3times mol hydrolyzable org. aluminum compd. based on 1mol hydrolyzable silicon compd., is added to water or the hydrous solvent having 5-9pH value to hydrolyze. The silica-alumina combined powder obtd. by the method above-mentioned is a spherical body having 0.1-1 $\mu$ m particle size. The partial hydrolyzate of org. silicon compd. is composed of monomer, dimer, trimer or oligomer of the org. silicon compd. The partial hydrolyzate of org. silicon compd. having about 0.1-10 composition ratio of dimer to monomer, is used.

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zu den Bibliographiedaten

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## TRANSLATION FROM JAPANESE

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(54) Title of the Invention: **Method for Manufacturing Silica-Alumina  
Composite**

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(22) Filing Date: February 3, 1988  
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## **SPECIFICATION**

### **1. Title of the Invention**

Method for Manufacturing Silica-Alumina Composite

### **2. Claims**

1. A method for manufacturing a silica-alumina composite, characterized in that a mixed solution comprising [i] a partial hydrolysate of a hydrolyzable organosilicon compound and [ii] a hydrolyzable organoaluminum compound in an amount of 0.3 to 3 molar multiples of said organosilicon compound is added to water or a water-containing solvent with a pH of 5 to 9 and hydrolyzed.

2. A manufacturing method as defined in Claim 1, wherein the silica-alumina composite consists of globules with a particle diameter of 0.1 to 1  $\mu\text{m}$ .

### **3. Detailed Description of the Invention**

#### **Field of Industrial Utilization**

The present invention relates to a method for manufacturing a silica-alumina composite that can be used as a starting material for sintered articles.

#### **Prior Art and Related Problems**

Mullite and other silica-alumina ceramics have low coefficients of thermal expansion and dielectric constants, and have therefore attracted attention in recent years as substrates for electronic materials. Starting material powders used for ceramic sintered articles such as the aforementioned substrates for electronic materials are also required to have adequate packing properties, sintering properties, purity, and the like. In addition, considerations related to packing properties and sintering properties require that such powders have a particle diameter of 0.1 to about 1  $\mu\text{m}$ , that is, in the submicron region.

Two types of methods have been suggested for obtaining such submicron powders. One of them is a so-called breakdown technique for pulverizing large particles, and the other is a so-called buildup technique for precipitating particles from solutions, for example. With the breakdown technique, however, contamination with impurities inevitably occurs because of the need to deal with small particle diameters in a so-called submicron region, making it impossible to obtain high-purity powders. As a result, powders that satisfy the aforementioned requirements are usually synthesized by buildup.

Known methods for synthesizing submicron silica-alumina composites by buildup include (1) precipitation from solutions, (2) hydrothermal synthesis, and (3) spraying/thermal decomposition. These methods have the following shortcomings, however.

First, precipitation from solutions (method 1), as described, for example, in Japanese Laid-Open Patent Application 58-156524, involves hydrolyzing a mixed solution comprising a hydrolyzable organosilicon compound and a hydrolyzable organic compound of aluminum in an alkaline solvent to synthesize a composite of silica and alumina. With this method, however, it is difficult to synthesize a silica-alumina composite containing a large amount of alumina.

Hydrothermal synthesis (method 2), which is reported by Watarimura et al. in *Yogyo Kyokaiishi* (Vol. 91, No. 6), requires considerable reaction time (two or more days) and cannot be considered commercially advantageous.

Spraying/thermal decomposition (method 3) is described by Imai et al. in *Reports of the Research Laboratory of Engineering Materials* (11, 1986). With this method, however, it is indispensable that sodium be present in order to obtain a silica-alumina composite, making it necessary for the sodium to be removed by post-synthesis ion exchange in order to obtain a pure silica-alumina composite, and hence requiring a complex manufacturing process.

#### Means Used to Solve the Aforementioned Problems

As a result of painstaking and repeated research aimed at addressing the aforementioned problems and developing a method for manufacturing a silica-alumina composite whose particle diameters lie in a submicron region, the inventors devised the present invention upon discovering the following method.

Specifically, the present invention resides in a method for manufacturing a silica-alumina composite powder characterized in that a mixed solution comprising (i) a partial hydrolysate of an organosilicon compound and (ii) a hydrolyzable organoaluminum compound in an amount of 0.3 to 3 molar multiples of said organosilicon compound is added to water or a water-containing solvent with a pH of 5 to 9 and hydrolyzed.

No particular restrictions are imposed on the organosilicon compound used in the present invention as long as it is a hydrolyzable compound, and any known compound may be used. An alkoxysilane expressed by the formula  $\text{Si}(\text{OR})_4$  is commonly suitable for use. The R in the formula is an alkyl group, and, under common conditions, is preferably a methyl group, ethyl group, propyl group, butyl group, or other lower alkyl group with a carbon number of 1 to 5.

An important condition of the present invention is that the organosilicon compound be partially hydrolyzed in advance, but no particular restrictions are imposed on the partial hydrolysate, and any hydrolyzable compound may be used.

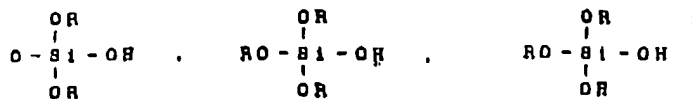
The aforementioned partial hydrolysate comprises an organosilicon compound monomer, a dimer or trimer obtained by condensing this monomer, or a higher oligomer. The partial hydrolysate considered optimal for use in the present invention is a compound in which the content of said dimer with respect to said monomer is 0.1 to 10, preferably 0.2 to 6, and ideally 0.25 to 4.

The aforementioned content is a typical numerical value representing the degree of partial hydrolysis. Commonly, a low degree of partial hydrolysis means that much of the monomer remains without undergoing polymerization during partial hydrolysis and that only a small amount of the dimer has been formed, resulting in a low content of the dimer in relation to the monomer. As partial hydrolysis proceeds further, the monomer is polymerized and consumed, whereas the dimer first increases to a certain point and then remains virtually constant. Consequently, the content of the dimer in relation to the monomer increases as partial hydrolysis progresses.

The aforementioned content can be measured by any means. Gas chromatography is commonly employed to measure the peak area of the dimer in relation to the peak area of the monomer. In this case, several peaks representing the monomer commonly appear over a short holding period (for example, 2 to 4 minutes), whereas several peaks representing the dimer appear over an extended holding period (for example, 4 to 9 minutes).

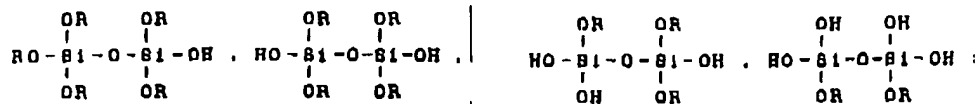
Although it is not yet clear why the monomer and dimer peaks separate into several units in such a manner, it can be assumed that the separation results from the fact that hydrolysates such as those shown below form when, for example, an alkoxysilane is used as an organosilicon compound.

(Paste group of three formulas here)



It can also be assumed that the dimer peaks separate into several units due, for example, to the formation of hydrolysates such as those shown below.

(Please paste group of four formulas here)



Known methods can be used to synthesize partial hydrolysates in accordance with the present invention, with no particular limitations imposed. The method suitable for use under ordinary conditions is one in which hydrolysis is performed after water and an organosilicon compound have been added to a solvent that dissolves both water and the organosilicon compound. Alcohols, ethers, and ketones can be cited as examples of solvents preferred for such use, with alcohols being especially preferable. Methanol, ethanol, propanol, butanol, and other such lower alcohols are preferred as such alcohols, with methanol being especially preferable for such use.

The amount in which water is used for the synthesis of the aforementioned partial hydrolysate is determined as needed because this amount varies with the conditions for partial hydrolysis. The amount of water should commonly be set to between 0.1 and 5 molar multiples, and preferably 0.5 and 3 molar multiples, of the organosilicon compound in order to achieve a value of 0.1 to 10 for the ratio of the dimer in relation to the monomer contained in the aforementioned partial hydrolysate.

An acid or an alkali can be used as a catalyst for such hydrolysis, but the use of an acid catalyst is preferred. No particular restrictions are imposed on such acid catalysts, and any known catalyst can be used. Of these, the following are preferred: hydrochloric acid, nitric acid, sulfuric acid, phosphoric acid, and other mineral acids; formic acid, acetic acid, malonic acid, and other organic acids; acid-type ion-exchange resins; and the like.

The organoaluminum compound used in the present invention is not subject to any particular limitations as long as it is hydrolyzable, and any known compound can be used. Common examples of suitable organoaluminum compounds include aluminum alkoxide compounds expressed by the formula  $\text{Al}(\text{OR}')_3$  (where  $\text{R}'$  is an alkyl group), and compounds in which all or part of the alkoxyl groups ( $\text{OR}'$ ) in the aforementioned formula have been substituted by carboxyl groups or  $\beta$ -dicarbonyl groups. Of the organoaluminum compounds described above, the following are particularly suitable: aluminum ethoxide, aluminum propoxide, aluminum butoxide, aluminum monobutoxydipropoxide, aluminum ethyl acetoacetate diisopropoxide, aluminum tris(ethyl acetoacetate), aluminum monoacetyl acetate bis(ethyl acetoacetate), aluminum tris(acetylacetone), and the like. Of these, organoaluminum compounds having dicarbonyl groups, as in aluminum ethyl acetoacetate diisopropoxide, are considered ideal for use. The amount of such an organoaluminum compound should be 0.3 to 3 molar multiples, preferably 0.5 to 2 molar multiples, and ideally 0.5 to 1.5 molar multiples, of the organosilicon compound. If the amount of the organoaluminum compound falls outside of the aforementioned range, it is impossible to obtain an adequately dispersed silica-alumina composite powder.

In the present invention, the hydrolyzable organoaluminum compound and a partial hydrolysate of an organosilicon compound must be premixed before being hydrolyzed. It is impossible to obtain particles in which silicon and aluminum are uniformly combined if the ingredients are added separately to water or a water-containing solvent without being premixed.

No particular restrictions are imposed on the methods for preparing a mixed solution of an organoaluminum compound and a partial hydrolysate of an organosilicon compound in accordance with the present invention. It is usually sufficient for the partial hydrolysate of an organosilicon compound or a solution thereof to be added to the organoaluminum compound or a solution thereof while the latter is agitated, although a reverse procedure may also be adopted. It is also possible to optionally add the organoaluminum compound and a partial hydrolysate of the organosilicon compound to the solvent in which they can be dissolved during agitation.

In the present invention, the solution for hydrolyzing the aforementioned mixed solution must be water or a water-containing solvent with a pH of 5 to 9, and preferably 5 to 7. If the pH of the solution falls outside of the aforementioned range, it is impossible to obtain an adequately dispersed silica-alumina composite powder, and the product sometimes forms a gel.

Water and an organic solvent compatible with water can be used without any limitations as components of the water-containing solvent of the present invention. Of these organic solvents, the following are suitable for use: methanol, ethanol, propanol, butanol,

ethylene glycol, diethylene glycol, glycerol, and other alcohols; tetrahydrofuran, dioxane, and other ethers; acetone, acetylacetone, and other ketones; and mixtures of the aforementioned organic solvents. Satisfactory powder dispersibility is obtained when the solvent is an alcohol. Furthermore, no particular restrictions are imposed on the amount of water in the water-containing solvent of the present invention, provided this amount is sufficient for hydrolyzing the mixed solution of the organoaluminum compound and the partial hydrolysate of the organosilicon compound. It is preferable, however, for this amount to be at least 10 wt%, and preferably at least 25 wt%, with respect to the water-containing solvent.

Although the present invention imposes no particular limitations on the methods for performing hydrolysis after adding a mixed solution of an organoaluminum compound and a partial hydrolysate of an organosilicon compound, it is preferable for the aforementioned mixed solution to be added in drops to water or a neutral water-containing solvent being agitated in order to hydrolyze the aforementioned mixed solution rapidly and uniformly in the water or neutral water-containing solvent.

#### Merits of the Invention

The above method makes it possible to obtain a high-purity silica-alumina composite that does not require removal of impurities by, for example, a technique such as ion-exchange following manufacture and that is contaminated only negligibly with other metal oxides or the like, and to form this silica-alumina composite into a globules having a particle diameter of 0.1 to 1  $\mu\text{m}$ . In addition, synthesis can be performed by varying the alumina content of the silica-alumina composite over a wide range.

Another merit is that a simple mixing vessel can be used as the manufacturing equipment of the present invention, eliminating the need for particularly complex equipment.

#### Practical Examples

The present invention will now be described in detail, but the present invention is not limited by these practical examples.

The following method was used to measure the content of dimers in relation to the monomer of the organosilicon compound in the partial hydrolysates used in the practical examples below. Specifically, GC-9A (manufactured by Shimadzu) equipped with an FID detector was used as a gas chromatograph, and helium was fed at a rate of 40 mL/min as carrier gas. A glass column with a length of 3 m was used, this column was packed with silicon GE, SE-30 (manufactured by Wako Pure Chemical), and measurements were performed at an injection temperature of 200°C and a column temperature of 130 to 180°C (the temperature was raised at a rate of 5°C/min following sample injection). Chromatograph E-13A (manufactured by Shimadzu) was used for peak detection.



### Practical Example 1

104 g tetraethyl silicate (manufactured by Nihon Korukoto) was dissolved in 250 mL methanol (manufactured by Wako Pure Chemical), 9 g of 0.1 N hydrochloric acid was added thereto, and the system was then agitated for 3 hours at 20°C. The solution was analyzed by the aforementioned gas chromatography, and it was found that the ratio of the dimer to the monomer in the solution was 2.8. This solution was added to a mixed solution comprising 206 g aluminum ethyl acetoacetate diisopropoxide (manufactured by Kawakyu Fine Chemical) and 250 mL ethanol, and the ingredients were then mixed. The resulting mixed solution was added in drops to a water-containing solvent comprising 0.8 L water and 0.8 L methanol, yielding a silica-alumina composite powder. This composite powder was observed under an electron microscope, and was found to consist of spherical particles measuring 0.1 to 0.7  $\mu\text{m}$ . According to the reading on a pH meter, the pH of the water-containing solvent was 5.7. Figure 1 shows an electron micrograph depicting the particle structure of the composite powder.

### Practical Example 2

104 g tetraethyl silicate was dissolved in 250 mL methanol, 18 g of 0.1 N nitric acid was added thereto, and the system was then agitated for 1.5 hours at 30°C. The solution was analyzed by the same method as in Practical Example 1, and it was found that the ratio of the dimer to the monomer in the solution was 3.7. This solution was added to a solution of 96 g aluminum ethyl acetoacetate diisopropoxide and 200 mL isopropanol (manufactured by Tokuyama Soda), and the ingredients were then mixed. The resulting mixed solution was added in drops under agitation to 1.5 L water, yielding a silica-alumina composite powder. This composite powder was observed under an electron microscope, and was found to consist of spherical particles measuring 0.1 to 0.7  $\mu\text{m}$ . According to the reading on a pH meter, the pH of the water was 5.4. Figure 2 shows an electron micrograph of the composite powder.

### Practical Example 3

104 g tetraethyl silicate was dissolved in 250 mL methanol, 9 g of 0.1 N hydrochloric acid was added thereto, and the system was then agitated for 30 minutes at 30°C. The solution was analyzed by the same method as in Practical Example 1, and it was found that the ratio of the dimer to the monomer in the solution was 0.5. This solution was added to a solution of 137 g aluminum ethyl acetoacetate diisopropoxide and 250 mL acetone, and the ingredients were then mixed. The resulting mixed solution was added in drops to a water-containing solvent comprising 1.2 L water and 0.3 L isopropanol, yielding a silica-alumina composite powder. This composite powder was observed under an electron microscope, and was found to consist of spherical particles measuring 0.2 to 0.6  $\mu\text{m}$ . According to the reading on a pH meter, the pH of the water-containing solvent was 5.5.

#### Practical Example 4

104 g tetraethyl silicate was dissolved in 250 mL methanol, 15 g of 1 N acetic acid was added thereto, and the system was then agitated for 2 hours at 30°C. The solution was analyzed by the same method as in Practical Example 1, and it was found that the ratio of the dimer to the monomer in the solution was 3.1. This solution was added to a solution of 137 g aluminum isopropoxide (manufactured by Kawakyu Fine Chemical) and 200 mL ethylene glycol, and the ingredients were then mixed. The resulting mixed solution was added in drops to a water-containing solvent comprising 0.8 L water and 0.8 L methanol, yielding a silica-alumina composite powder. This composite powder was observed under an electron microscope, and was found to consist of spherical particles measuring 0.2 to 0.8  $\mu\text{m}$ .

#### Practical Example 5

76 g tetramethyl silicate was dissolved in 250 mL methanol, 9 g of 0.1 N hydrochloric acid was added thereto, and the system was then agitated for 30 minutes at 30°C. The solution was analyzed by the same method as in Practical Example 1, and it was found that the ratio of the dimer to the monomer was 6.1. This solution was added to a solution of 137 g aluminum ethyl acetoacetate diisopropoxide and 250 mL ethanol, and the ingredients were then mixed. The resulting mixed solution was added in drops to a water-containing solvent comprising 0.8 L water and 0.8 L methanol, yielding a silica-alumina composite powder. This composite powder was observed under an electron microscope, and was found to consist of spherical particles measuring 0.1 to 0.5  $\mu\text{m}$ .

#### Comparative Example 1

104 g tetraethyl silicate was dissolved in 250 mL methanol, the resulting solution was added to a solution of 206 g aluminum ethyl acetoacetate diisopropoxide and 250 mL ethanol, and the ingredients were then mixed. The resulting mixed solution was added in drops to a water-containing solvent comprising 0.8 L water and 0.8 L methanol, yielding a gelled product.

#### Comparative Example 2

104 g tetraethyl silicate was dissolved in 250 mL methanol, 9 g of 0.1 N hydrochloric acid was added thereto, and the system was then agitated for 1 hour at 30°C. This solution was added to a solution of 206 g aluminum ethyl acetoacetate diisopropoxide and 250 mL ethanol, and the ingredients were then mixed. The resulting mixed solution was added in drops to a water-containing solvent comprising 0.8 L methanol and 0.8 L of a 0.1 N aqueous solution of hydrochloric acid, yielding a gelled product. According to the indication of pH test paper, the pH of the water-containing solvent was one or lower.

### Comparative Example 3

104 g tetraethyl silicate was dissolved in 250 mL methanol, 9 g of 0.1 N hydrochloric acid was added thereto, and the system was then agitated for 1 hour at 30°C. This solution was added to a solution of 206 g aluminum ethyl acetoacetate diisopropoxide and 250 mL ethanol, and the ingredients were then mixed. The resulting solution was added in drops to a water-containing solvent comprising 0.75 L methanol, 0.71 L water, and 38 mL aqueous ammonia (ammonia content; 25%; manufactured by Wako Pure Chemical), yielding a gelled product. According to the indication of pH test paper, the pH of the water-containing solvent was higher than 11.

### Comparative Example 4

104 g tetraethyl silicate was dissolved in 250 mL methanol, 9 g of 0.1 N hydrochloric acid was added thereto, and the system was then agitated for 1 hour at 30°C. This solution was added to a solution of 206 g aluminum ethyl acetoacetate diisopropoxide and 250 mL ethanol, and the ingredients were then mixed. The resulting solution was added in drops to a water-containing solvent comprising 0.8 L water and 0.8 L methanol, yielding a gelled product.

#### 4. Brief Description of the Drawings

Appended Figures 1 and 2 are electron micrographs showing the particle structures of the silica-alumina composites obtained in Practical Examples 1 and 2, respectively.

Figure 1



Figure 2

